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(54) Title: POLY(1,4-CYCLOHEXYLENEDIMETHYLENE TEREPHTHALATE) WITH IMPROVED MELT STABILITY (57) Abstract Disclosed are reinforced polyester compositions having repeat units from terephthalic acid and 1,4-cyclohexanedimethanol which have improved melt stability due to the addition of small amounts of an epoxy compound and either a phosphite or phosphonite.		

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POLY(1,4-CYCLOHEXYLENEDIMETHYLENE TEREPHTHALATE)
WITH IMPROVED MELT STABILITY

Technical Field

5 This invention relates to poly(1,4-cyclohexylene-
dimethylene terephthalate) containing additives which
improve molecular weight retention without branching
after exposure to melt temperatures. The additives are
10 (a) an epoxy compound and (b) a phosphite or phosphonite
wherein at least one of the P-O bonds is attached to an
aryl radical. The compositions are useful in injection
molding, particularly of glass fiber reinforced and
flame retarded products for the electrical and
electronics industry.

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Background of the Invention

Thermoplastic polyesters, such as poly(ethylene
terephthalate) [PET], poly(butylene terephthalate)
[PBT], and poly(1,4-cyclohexylenedimethylene
20 terephthalate) [PCT] are useful as injection molding
compounds for a variety of applications. In general
these materials are reinforced with glass fiber or
mineral fillers to enhance properties. Applications
include automotive parts, appliance parts, and
25 electrical-electronics parts. The reinforced
thermoplastic polyesters have useful combinations of
strength, heat resistance and chemical resistance for
these uses. In many cases it is required that the
material also be flame-retarded, and thermoplastic
30 polyesters can be successfully flame retarded through
the use of a number of known flame-retarding additives.

Many times the thermoplastic polyester is
processed into the final article of interest by
injection molding. In the injection molding process, a

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quantity of material is melted but only a portion of it is injected into the mold. It is possible that material will remain in the melt in the molding machine for several minutes (perhaps fifteen minutes) before it is
5 injected and cooled. For this reason, it is desirable for the polymer to have excellent stability so that it will maintain high molecular weight even after several minutes holding time at melt temperatures. Maintaining high molecular weight (or I.V.) is important in
10 maintaining mechanical properties such as tensile, impact and flexural strengths.

This problem of melt stability is especially significant for PCT because of its higher melting temperature (290°C vs 250°C for PET and 225°C for PBT).
15 The higher melting temperature means that the polymer must be processed at a higher temperature, which accelerates the degradation rate.

One method to maintain the molecular weight at melt temperatures is to compound reactive additives into the
20 formulation. Useful known additives of this type are multifunctional epoxy compounds and oligomers or polymers produced from them. These additives help maintain molecular weight by reacting with polyester chain ends. Because the additives are multifunctional,
25 however, they will also result in chain branching. Thus an initially linear thermoplastic polyester, after stabilization with the multifunctional additive and exposure to melt conditions, will be branched. This is an undesirable result because it leads to changing flow
30 characteristics and irreproducible processing and mechanical properties.

Branching can be controlled by the use of phosphorous-based stabilizers in conjunction with the reactive epoxy compounds. In some cases, however,

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branching is controlled at the expense of melt stability; i.e. the effectiveness of the reactive epoxy-based compound is compromised. Unexpectedly, it has been found that a certain class of phosphorous stabilizers will allow branching to be controlled without unacceptable loss of melt stability.

The use of certain epoxy compounds in PCT is disclosed in European Patent Application 0 273 149. This application also discloses the use of a phosphate compound as a component of a formulation. Phosphates are not within the scope of the present invention. The use of phenoxy resin, an epoxy-based polymer, in PET and other thermoplastic polyesters is known by others.

15 Description of the Invention

According to the present invention there is provided a polyester molding composition with improved stability in the melt comprising

- 20 a) a polyester containing repeating units from terephthalic acid and 1,4-cyclohexane-dimethanol and having an inherent viscosity from 0.5 to 1.0,
- b) 0.1-5%, preferably 0.5-1%, by weight of the total composition of a multifunctional epoxy-based or epoxy-derived compound,
- 25 c) 0.1-1.0%, preferably 0.25-0.5%, by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds is attached to an aryl radical.

30 In a preferred embodiment of the present invention there is provided a reinforced molding composition with improved stability in the melt comprising

- a) a polyester having repeating units from a dicarboxylic acid component and a glycol

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- component, at least 90 mol % of said acid component being terephthalic acid and at least 90 mol % of said glycol component being 1,4-cyclohexanedimethanol, said polyester
- 5 having an inherent viscosity from 0.5 to 1.0,
- b) 10-50% by weight of the total composition of a reinforcing material comprising glass fibers,
- c) 0.1-5% by weight of the total composition of a multifunctional epoxy compound, and
- 10 d) 0.1-1.0% by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds is attached to an aryl radical.

Also in a preferred embodiment of the invention

15 there is provided a flame-retarded, melt stable compound wherein the flame retardant additives comprise an organic bromine compound and an antimony compound.

The polyester, poly(1,4-cyclohexylenedimethylene terephthalate) contains repeat units from a dicarboxylic acid component and a glycol component. The dicarboxylic acid component, a total of 100 mol %, is at least

20 90 mol % terephthalic acid and the glycol component, a total of 100 mol %, is at least 90 mol % 1,4-cyclohexanedimethanol.

25 The dicarboxylic acid component may contain up to 10 mol % of other conventional aromatic, aliphatic or alicyclic dicarboxylic acids such as isophthalic acid, naphthalenedicarboxylic acid, cyclohexanedicarboxylic acid, succinic acid, sebacic acid, adipic acid, glutaric acid, azelaic acid and the like.

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The glycol component may contain up to 10 mol % of other conventional aliphatic or alicyclic glycols such as diethylene glycol, triethylene glycol, ethylene

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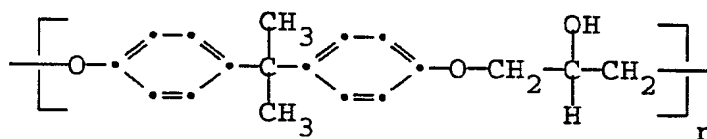
glycol, propanediol, butanediol, pentanediol, hexanediol, and the like.

The polyesters useful in this invention can be prepared by conventional polycondensation processes well known in the art. For example, the polyesters can be prepared by direct condensation of terephthalic acid or ester interchange using dimethyl terephthalate. The essential components of the polyester, e.g., terephthalic acid or dimethyl terephthalate and 1,4-cyclohexanedimethanol are commercially available.

The polyesters and copolyesters described above should have an I.V. (inherent viscosity) of from 0.5 to 1.0, and a melting point of at least 265°C.

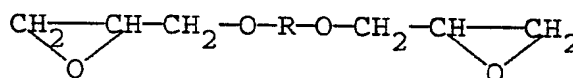
The epoxy compound used in the present invention is selected from

- 1) aromatic hydrocarbon compounds having at least 3 epoxide groups, including monomers, oligomers or polymers of up to 10 monomer units
- 2) polymers derived from a diepoxide monomer of the formula



wherein n is 50 to 200, or

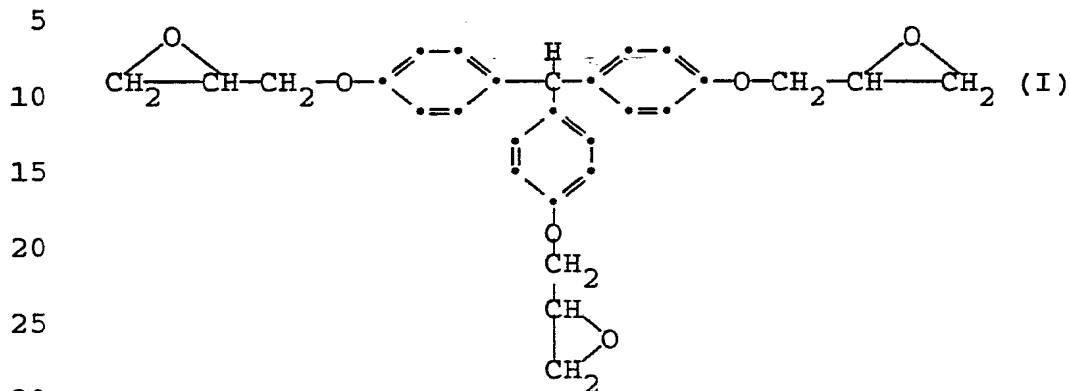
- 3) oligomers having 2 to 15 repeat units of diglycidyl ethers having the formula



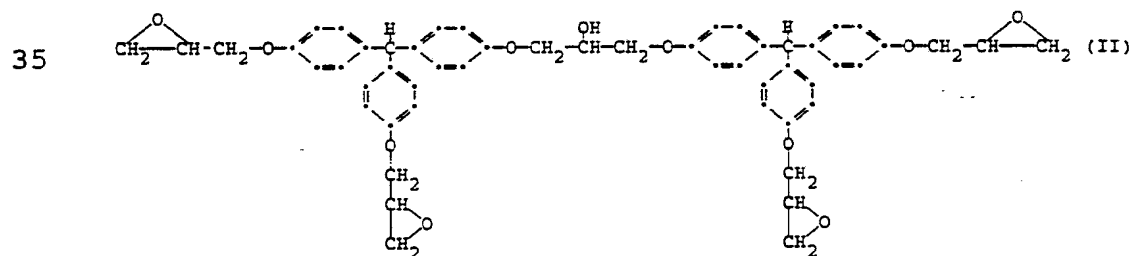
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wherein R is an aromatic radical of 6-15 carbon atoms.

Preferably, the compounds of 1) above have the structural formula



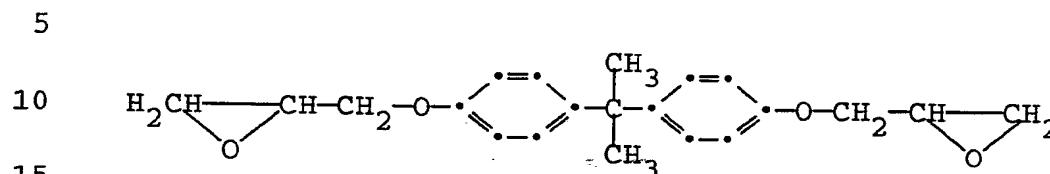
or



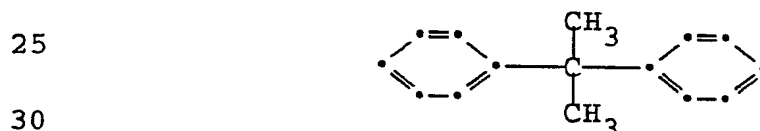
or are the reaction products of up to five moles of compound I with one mole of compound II. Commercially available compounds described in 1) include epoxylated novolac, tris(4-glycidyloxyphenyl)methane and polymers thereof, available from Dow Chemical Company.

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The diepoxide monomer referred to in 2) above has the structural formula



20 Preferably R in 3) above is



35 Examples of polymers described in 2) above include the polyhydroxyether of bisphenol A (commonly known as phenoxy) which is produced from 2,2'-bis(4-hydroxy-phenyl) propane and epichlorohydrin. Preparation of

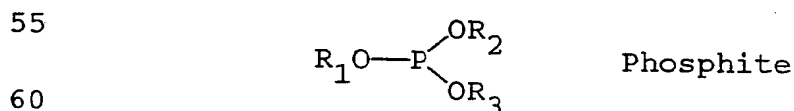
40 such polymers is described in U.S. Patent No. 3,356,646.

Commercially available compounds described in 3) include Epon oligomers of diglycidyl ether, available from Shell Chemical Company. These compounds have two

45 reactive epoxy groups and at least one secondary hydroxyl group per molecule.

The phosphorous-based compound is either a phosphite or a phosphonite, wherein at least one of the P-O bonds is attached to an aryl radical. Such

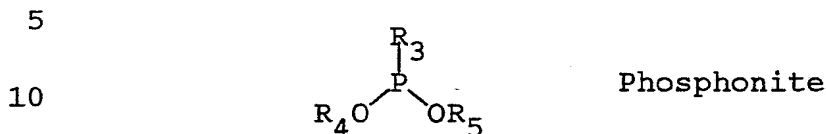
50 compounds may be represented by the formulas



where at least one of R₁, R₂ and R₃ is an aryl radical

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of 6 to 30 carbon atoms and any other(s) of R_1 , R_2 and R_3 are H or alkyl of 1 to 30 carbon atoms, or



15 where at least one of R_3 , R_4 and R_5 is an aryl radical of 6 to 30 carbon atoms and any other(s) R_1 , R_2 and R_3 are H or alkyl of 1 to 30 carbon atoms.

20 Examples of such materials are Ultrinox 626 phosphite, Ultrinox 633 phosphite, (General Electric Chemicals), Irgafos 168 phosphite (Ciba-Geigy Corporation), Ethanox 398 phosphonite (Ethyl Corporation) and Sandostab P-EPQ phosphonite (Sandoz

25 Chemicals).

The flame retardant comprises an aromatic organic compound having at least one aromatic ring having halogen bonded directly to the aromatic ring. The halogenated compounds are preferably brominated or

30 chlorinated, and most preferably, brominated. The bromine content, when bromine is present, is at least 25% of the weight of the compound, and the chlorine content, when chlorine is present, is at least 40% of the weight of the compound. In addition, the flame-

35 retardant compound should be substantially stable at up to 300°C and should not cause degradation of polyester. When the compound contains bromine, the amount of the bromine present in the blend should preferably be between 2-12% by weight of blend, and most preferably

40 5-10%. When the compound contains chlorine, the amount of the chlorine present should preferably be 3-20% by weight of blend and most preferably 5-12%. Representative of such compounds are decabromodiphenyl ether, octabromodiphenyl ether, ethylene bis-(tetra-

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bromophthalimide), brominated polystyrene, poly(dibromophenylene oxide), the condensation product of two moles of tetrachlorocyclopentadiene and one mole of cyclooctadiene, and the like. Polymeric retardants may
5 have molecular weight up to 200,000 or more.

The flame retardant also comprises an antimony compound, for example, antimony oxide, sodium antimonate, or powdered antimony metal. The amount of antimony compound should be between 2 and 10% of the
10 weight of the total composition, preferably between 3 and 6%.

A preferred reinforcing filler is glass fibers which may be introduced into the composition as chopped glass fibers or continuous glass fiber rovings in
15 amounts of 10-50% by weight of the composition. Other reinforcing materials such as metal fibers, graphite fibers, aramid fibers, glass beads, aluminum silicate, asbestos, mica, talc and the like may be used in combination with, or in place of the glass fibers.

Substantially any of the types of glass fibers generally known and/or used in the art are useful in the present invention. Typical types are those described in British Patent No. 1,111,012, U.S. Patent No. 3,368,995 and German Auslegeschrift No. 2,042,447. Thus, the
20 average length of useful fibers covers a wide range, for example, 1/16 to 2 inches (0.16-5.1 cm). The presently preferred glass fibers have an average length of 1/16 to 1/4 inch (0.16-0.64 cm).

Glass filaments made of calcium-aluminum-boron
30 silicate glass, which is relatively free from sodium carbonate, are preferably used. Glass of this type is known as "E" glass; however, where the electrical properties of the reinforced polyesters are not important, other glasses can also be used, for example

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the glass with a low sodium carbonate content which is known as "C" glass. The diameters of the filaments can be in the range from 0.003 to 0.018 mm, but this is not critical for the present invention.

5 In addition to the components discussed hereinabove, the blends of this invention may contain additives commonly employed with polyester resins, such as colorants, mold release agents, antioxidants, tougheners, nucleating agents, crystallization aids,
10 plasticizers, ultraviolet light and heat stabilizers and the like.

 The blends of this invention are prepared by blending the components together by any convenient means to obtain an intimate blend. Compounding temperatures
15 must be at least the melting point of the PCT. For example, the polyester can be mixed dry in any suitable blender or tumbler with the other components and the mixture melt-extruded. The extrudate can be chopped. If desired the reinforcing material can be omitted
20 initially and added after the first melt extrusion, and the resulting mixture can then be melt extruded. The product is especially suitable as an injection molding material for producing molded articles.

25 Examples

 The glass fiber reinforced (GFR) PCT blends of this work were prepared by extrusion compounding using a 1.5 inch Sterling single screw extruder (L/D = 36/1) at temperatures of 300°C. The resulting pellets were
30 injection molded into tensile and flexural bars for use in mechanical and flammability property testing. Melt stability was determined on these blends by drying a small sample of the compounded pellets in vacuum oven overnight at 80°C. The dried pellets were then loaded

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into a Tinius Olsen melt indexer and held for 15 minutes at 300°C. Molecular weight analysis was done on both the compounded pellets and the samples that were exposed to 300°C melt temperatures for 15 minutes by gel permeation chromatography. The melt stability of these blends was shown by the retention of weight-average molecular weight (Mw) at 300°C for 15 minutes (see Table 1).

Good melt stability is characterized by a loss of less than 15% of the original Mw, after exposure for 15 minutes, the original Mw being defined as that at zero time. The degree of branching is characterized by the ratio of the weight-average molecular weight (Mw) to the number average molecular weight (Mn), Mw/Mn. This value should be less than 2.0 after the fifteen minute melt exposure. Values above 2.0 indicate that the composition is undergoing branching.

Blend A is described as follows. Percentages are by weight of the total composition. There is no phosphorus compound.

48% PCT polyester
30% Owens Corning 492AA glass fibers
3.75% Benzoflex S312 neopentyl glycol dibenzoate
0.25% Irganox 1010 stabilizer
12% Pyrochek 68PB brominated polystyrene
5% Thermogard FR sodium antimonate
0.5% Polywax 1000 polyethylene (M.W. = 1000)
0.5% Dow XD9053.01 epoxy resin (polymer of tris(4-glycidyloxyphenyl) methane

Blend A, had excellent mechanical and flammability properties. This blend had good retention of Mw after 15 minutes at 300°C, but it also had undesirable branching as shown by the Mw/Mn ratio of 3.34.

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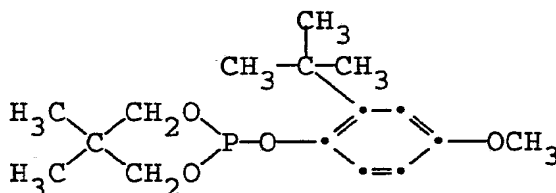
Blends B, C, D, and E had the same composition as Blend A, but with 0.25% of either Ultrinox 626 phosphite, Ultrinox 633 phosphite, Irgafos 168 phosphite, or BHA/NPG phosphite of the formula,

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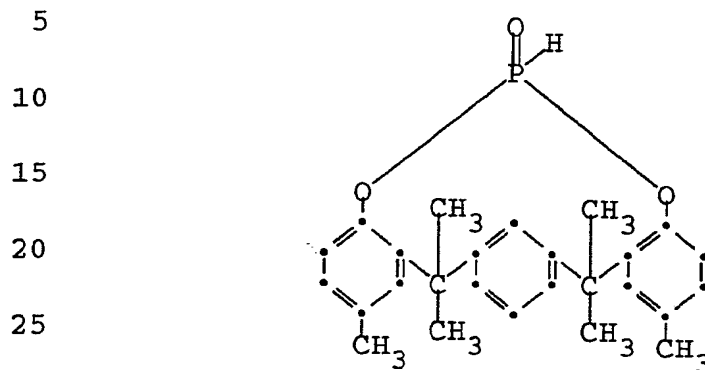
respectively. These materials were all phosphites in which at least one P-O bond was attached to an aryl radical represented by the formula given hereinbefore. These blends had excellent mechanical and flammability properties. These blends also had excellent retention of Mw after 15 minutes at 300°C without undesirable branching as shown by Mw/Mn ratios less than 2.0.

Blends F and G had the same composition as Blend A, but with a 0.25% of Sandostab P-EPQ phosphonite and Ethanox 398 phosphonite, respectively. These materials were either phosphonites or fluorine-containing phosphonites in which at least one P-O bond was attached to an aryl radical represented by the formula given hereinbefore. These blends also had excellent mechanical and flammability properties. These blends also had excellent retention of Mw after 15 minutes at 300°C without the undesirable branching as shown by the Mw/Mn ratios less than 2.0.

Blends H and I had the same composition as Blend A, but with 0.25% of Weston 619 phosphite and Weston TSP phosphite, respectively. These added materials were aliphatic phosphites. These blends had excellent mechanical and flammability properties, but had poor retention of Mw after 15 minutes at 300°C.

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Blend J had the same composition as Blend A, but with a 0.25% of a phosphonate of the formula



30 This blend had excellent mechanical and flammability properties, but had poor retention of Mw after 15 minutes at 300°C.

Blend K is described as follows. Percentages are by weight of the total composition. There is no phosphorus compound.

35 45,5% PCT polyester
 30% glass fibers
 3.75% Benzoflex S312 neopentyl glycol dibenzoate
 40 0.25% Irganox 1010 stabilizer
 13% Great Lakes PO-64P polydibromophenylene oxide
 5% Thermogard FR sodium antimonate
 0.5% Polywax 1000 polyethylene (M.W. = 1000)
 45 2% Phenoxy PKHH polyhydroxyether of bisphenol A

Blend K had good mechanical and flammability properties. This blend had excellent retention of Mw after 15 minutes at 300°C, but had undesirable branching as shown by the Mw/Mn ratio of 2.89.

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Blend L had the same composition as Blend K, but with a 0.25% of barium sodium organophosphate. This blend had good mechanical and flammability properties, but poor retention of Mw after 15 minutes at 300°C.

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TABLE 1

Melt Stability at 300°C of Flame Retarded
Glass Reinforced PCT Blends

<u>Example</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Mn	0 minutes	24518	25918	25231	25615	26375
	15 minutes	18246	21074	20999	20984	20230
Mw	0 minutes	46097	43557	43745	42547	44658
	15 minutes	40867	40016	38667	41382	39178
Mw/Mn	0 minutes	1.88	1.68	1.73	1.66	1.69
	15 minutes	3.34	1.90	1.84	1.98	1.94

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<u>Example</u>	<u>G</u>	<u>H</u>	<u>I</u>	<u>J</u>	<u>K</u>	<u>L</u>
Mn	0 minutes	25868	25212	25947	26489	26176
	15 minutes	20503	17152	19635	19202	14758
Mw	0 minutes	43181	41344	43715	42672	45914
	15 minutes	39036	30980	36164	33627	42712
Mw/Mn	0 minutes	1.67	1.64	1.68	1.61	1.75
	15 minutes	1.90	1.81	1.84	1.75	2.89

1.76
2.03

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The above examples demonstrate that, unexpectedly, only organic phosphites and phosphonites in which at least one of the P-O bonds is attached to an aryl radical are effective in providing a useful combination of melt stability and control of branching.

Unless otherwise specified, all parts, percentages, ratios, etc., are by weight.

Molecular weights are determined in conventional manner using gel permeation chromatography.

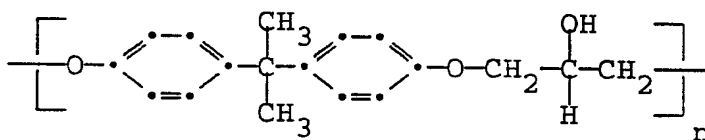
Inherent viscosity (I.V.) is measured at 25°C using 0.50 gram of polymer per 100 mL of a solvent consisting of 60 percent by weight phenol and 40 percent by weight tetrachloroethane.

While the invention has been described in detail with particular reference to preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

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CLAIMS

1. A polyester molding composition having improved melt stability characterized as a mixture of
 - a) a polyester having repeat units from terephthalic acid and 1,4-cyclohexane-dimethanol, said polyester having an I.V. of 0.5-1.0,
 - b) 10-50% by weight of the total composition of a reinforcing material comprising glass fibers,
 - c) 0.1-5% by weight of the total composition of a multifunctional epoxy based or epoxy derived compound, and
 - d) 0.1-1.0% by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds thereof is attached to an aryl radical having 6-30 carbon atoms.
2. A polyester molding composition having improved melt stability according to Claim 1 wherein said epoxy compound is selected from
 - a) aromatic hydrocarbon compounds having at least 3 epoxide groups, including monomers, oligomers or polymers of up to 10 monomer units
 - b) polymers derived from a diepoxide monomer of the formula



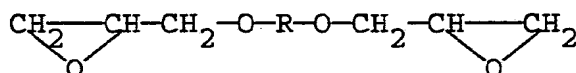
wherein n is 50 to 200, and

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- c) oligomers of diglycidyl ethers having the formula

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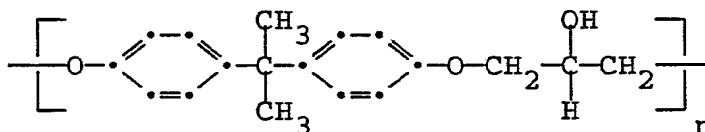
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wherein R is an aromatic radical of 6-15 carbon atoms.

3. A polyester molding composition according to Claim 2 wherein said epoxy compound is an aromatic hydrocarbon compound having at least 3 epoxide groups, including monomers, oligomers, or polymers of up to 10 monomer units
4. A polyester molding composition according to Claim 2 wherein said epoxy compound is a polymer derived from a diepoxide monomer of the formula

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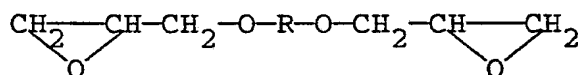
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wherein n is 50 to 200.

5. A polyester molding composition according to Claim 2 wherein said epoxy compound is an oligomer of a diglycidyl ether having the formula

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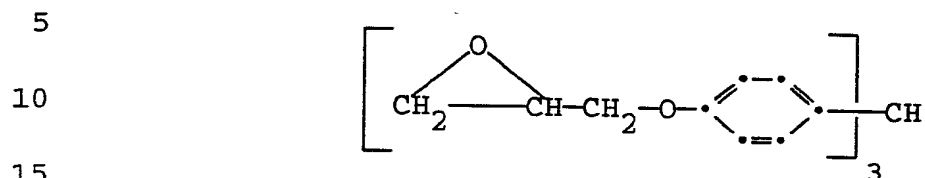
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wherein R is an aromatic radical of 6-15 carbon atoms.

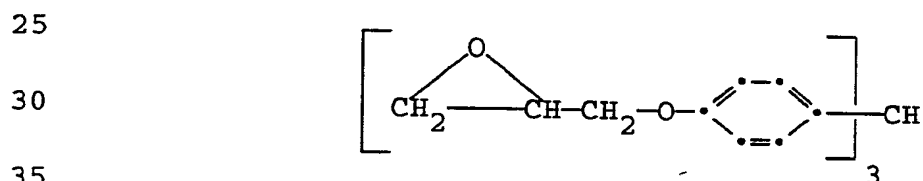
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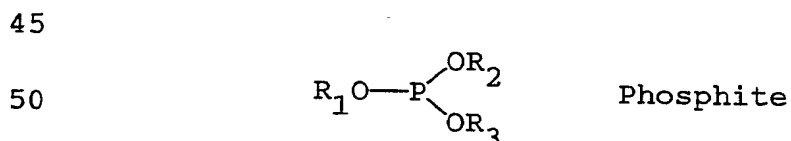
6. A polyester molding composition according to Claim 2 wherein said epoxy compound has the formula



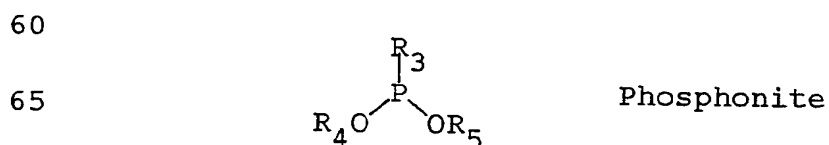
7. A polyester molding composition according to Claim 2 wherein said epoxy compound is an oligomer or polymer of up to 10 monomer units of the formula



- 40 8. A polyester molding composition according to Claim 1 wherein said phosphite or phosphonite compound has the formula



55 wherein at least one of R_1 , R_2 and R_3 is an aryl radical having 6 to 30 carbon atoms and any other of R_1 , R_2 and R_3 are H or alkyl of 1 to 30 carbon atoms, or

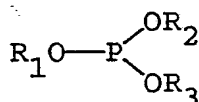


wherein at least one of R_3 , R_4 and R_5 is an aryl

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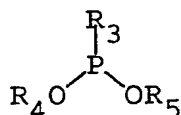
radical of 6 to 30 carbon atoms and any other is H or alkyl of 1 to 30 carbon atoms.

9. A polyester molding composition according to Claim 1 wherein the phosphite or phosphonite compound is a phosphite of the formula



wherein at least one of R_1 , R_2 and R_3 is an aryl radical having 6 to 30 carbon atoms and any other of R_1 , R_2 and R_3 are H or alkyl of 1 to 30 carbon atoms.

10. A polyester molding composition according to Claim 1 wherein said phosphite or phosphonite compound is a phosphonite having the formula



wherein at least one of R_3 , R_4 and R_5 is an aryl radical of 6 to 30 carbon atoms and any other is H or alkyl of 1 to 30 carbon atoms.

11. A polyester molding composition according to Claim 1 wherein said polyester contains repeat units from at least 90 mol % terephthalic acid and at least 90 mol % 1,4-cyclohexanedimethanol.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/05832

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ C 08 K 13/04, C 08 L 67/02, //(C 08 K 13/04, 5:15, 5:526, 7:14), (C 08 K 13/04, 5:15, 5:5393, 7:14) ./.		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 08 K, C 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP, A, 0273149 (GENERAL ELECTRIC CO.) 6 July 1988 see claims 1-6,10 cited in the application --	1-11
Y	GB, A, 1422278 (GENERAL ELECTRIC CO.) 21 January 1976 see claims 1-4,11,17; page 8, example 8 -----	1-11
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
	- 1. 02. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px 5px; margin-right: 10px;">E.P.O.</div> <div style="text-align: right;">M. 223</div> </div>	

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 90/0583

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : (C 08 L 67/02, 63:00)								
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black;">Classification System</th> <th style="width: 70%; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="height: 40px; vertical-align: top; border-right: 1px dashed black; border-bottom: 1px solid black;">IPC⁵</td> <td style="border-bottom: 1px solid black;"></td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵			
Classification System	Classification Symbols							
IPC ⁵								
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="width: 60%; border-bottom: 1px solid black;">Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="height: 300px;"></td> <td></td> <td></td> </tr> </table>			Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³			
Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³						
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>								
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center;">23rd January 1991</div> </td> <td style="width: 50%; border-bottom: 1px solid black; vertical-align: top;"> Date of Mailing of this International Search Report </td> </tr> <tr> <td style="border-bottom: 1px solid black; vertical-align: top;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; vertical-align: top;"> Signature of Authorized Officer </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">23rd January 1991</div>	Date of Mailing of this International Search Report	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer		
Date of the Actual Completion of the International Search <div style="text-align: center;">23rd January 1991</div>	Date of Mailing of this International Search Report							
International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer							

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9005832

SA 41176

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/01/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0273149	06-07-88	JP-A- 63221159	14-09-88
GB-A- 1422278	21-01-76	US-A- 3886104	27-05-75
		AU-A- 6373873	19-06-75
		CA-A- 1019080	11-10-77
		DE-A- 2400098	18-07-74
		FR-A, B 2213311	02-08-74
		JP-A- 49099743	20-09-74
		NL-A- 7400065	09-07-74